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ON THE LOW TEMPERATURE CHEMISTRY
PRECEDING END GAS AUTOIGNITION

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On the Low Temperature Chemistry Preceding End Gas Autoignition

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Abstract

A comparison is made between measured species concentrations in a spark ignition engine and predictions from a numerical model using detailed chemical kinetics. Gas samples are extracted from the end gas at times just prior to autoignition of n-butane/air or iso-butane/air mixtures. Concentration histories of stable species are obtained through gas chromatographic analysis. A detailed chemical kinetics model is used to predict species concentrations in an idealized end gas. The chemical reactions leading to formation of the relevant species are identified. The relative distribution of intermediate products predicted by the model is in good agreement with the experimental measurements. Chemical kinetic differences between autoignition of n-butane, a straight chain hydrocarbon, and iso-butane, a branched chain hydrocarbon, are discussed.

INTRODUCTION

For many years the problem of end-gas autoignition leading to knock was adequately controlled by the use of tetraethyl lead, and there was only moderate interest in understanding the fundamental phenomena behind this problem. Since statutory restrictions have severely curtailed the use of lead in automotive fuels, engine designers and fuel producers have had to resort to other methods to prevent the adverse effects of knock. Lower compression ratios, ignition control systems, complex means of fuel/air preparation, and expensive fuel refining and blending techniques have been satisfactory, at least in the short term, for controlling autoignition and knock in engines burning lead-free fuel. However, the next generation of improvements in fuel economy and performance may well require an increase in compression ratio which is now limited by knock.

End-gas autoignition involves processes which fall into two categories. The first includes fluid and thermal transport processes which are strongly coupled to the specific characteristics of the engine. The second category is much less dependent on the engine design and concerns the chemistry of low temperature oxidation of the fuel. In the present study, we focus our attention on these chemical processes. Specifically, our goal is to develop a comprehensive understanding of the basic chemistry that occurs in the compressively-heated end gas and can result in autoignition and knock in a spark-ignition engine.

In an earlier paper [1] we described the basic experimental and modeling aspects of our study of autoignition and knock in an engine. The results of this first effort pointed out the need to measure the concentrations of some of the intermediate species produced during the oxidative breakdown of the fuel. This is needed to verify the adequacy of

the chemical kinetic mechanism used in the computer modeling of the autoignition.

The concept of using gas sampling to investigate the low temperature chemistry occurring in the compressively-heated end gas is certainly not new. Fifty years ago, Egerton, Smith and Ubbelohde [2] employed a fast-acting sampling valve to make time resolved measurements of major species concentrations present in the end gas of a "knocking" engine. Their interpretation of the experimental data led to a conclusion that knock was due to an acceleration of the flame in the end gas. This work was carried out for fuels to which both pro- and anti-knock additives had been added. Fifteen years later in 1951, Downs, Walsh, and Wheeler [3] published a classic study of the chemistry that leads to knock in an engine. A large portion of this investigation was based on the use of time-resolved gas sampling and chromatographic analysis. This work was quite comprehensive and represented a significant step forward in understanding of peroxide formation in the end gas. Even today this study represents the foundation of the current thinking on the subject of end-gas autoignition and knock in an engine.

Over the next thirty-five years a number of other investigations of end-gas chemistry were published which were based on the use of some form of gas sampling technology. Some employed continuous sampling of the exhaust of a motored engine [4], while others used time-resolved in-cylinder sampling techniques -- either cycle averaged [5,6,7] or single cycle resolved [8]. These more recent studies essentially focused on the same issues addressed by the earlier work. However, advances in the technology of gas analysis improved the experimental methodology and allowed for a broader range of experimental conditions, fuels, additives

and intermediate species to be investigated. Downs, Griffiths and Wheeler [5] extended their earlier work [3] and from these observations, defined a distinction between single- and two-stage chemical processes leading to knock -- this classification being dependent upon the chemical characteristics of the fuel. The two-stage process is characterized by a low temperature first stage where cool flame chemistry predominates and the organic peroxides are the important intermediates. During the second or high temperature stage, hydrogen peroxide is an important intermediate, which was found to be strongly affected by the addition of tetraethyl lead.

The early gas-sampling investigations, described above provided, interesting insight into the end-gas chemistry preceding autoignition. Although these studies identified many of the critical intermediate species, lack of the capability to model the details of the chemical kinetics left some doubt as to whether all the important intermediates had been considered and which steps in the chemical mechanism were the most critical paths to the autoignition of the end gas. The currently available capability to model the detailed chemical kinetics with high speed computers now provides a powerful means of interpreting the results of the gas-sampling measurements, which could lead to a better understanding of the autoignition process. In the present work, gas sampling and chromatographic analysis is used to measure, just prior to autoignition or flame arrival, the concentrations of the stable intermediate species in the end gas of a research engine operated under knocking and nonknocking conditions. These results are then compared with the predictions of our kinetic model and the general trends from this comparison are interpreted in terms of the overall validity of the reaction mechanism.

EXPERIMENTAL

The experimental phase of this investigation was performed using a spark-ignition research engine. High swirl and multi-point ignition isolated the end gas in the center of the combustion chamber where it was confined on the sides by the propagating flame and on the top and bottom by the cylinder head and piston, respectively. This configuration prevents the combustion chamber walls from significantly influencing the end gas during compressive heating prior to autoignition. The amount of end gas autoigniting is experimentally controlled by the inlet manifold temperature and pressure. Cycle-to-cycle variation is reduced to a low level by using a skip-fire strategy -- in this case firing every third cycle. By configuring the experiment in this way, the engine could be operated at a knocking condition which was easily controlled and satisfactorily repeatable on a cycle-to-cycle basis. This repeatability is in contrast to many engines where knock occurs at random cycles and various locations in the cylinder. The details of the experimental configuration are available in a previous paper [9].

Experimental data for knocking operation with n-butane/air mixtures were obtained for the conditions of 600 rpm, spark ignition at top dead center (TDC), inlet manifold temperature and pressure of 160°C and 1.53 atm, and stoichiometric mixture ratio. These conditions resulted in the autoignition of about 40 percent of the initial fuel/air mixture at a time 3.2 ms after spark ignition and were the same as those for which the temperature and pressure histories had been measured previously [1]. For the nonknocking operation with n-butane, the same conditions as listed above were used, with the exception that the manifold pressure was reduced to 1.20 atm. When iso-butane was run under knocking conditions, the engine

control variables were 600 rpm, spark ignition at TDC, inlet manifold temperature and pressure of 210 °C and 1.79 atm, and stoichiometric mixture ratio; under these conditions, autoignition occurred 4.0 ms after spark ignition with 15 to 20 percent of the initial fuel/air mixture autoigniting. Nonknocking iso-butane data were collected by lowering the inlet temperature to 190°C, with all other operating conditions constant.

To obtain the time resolved, cycle-averaged samples of end gas from the combustion chamber, a fast acting, magnetically-actuated sampling valve was used. This valve, which was designed and constructed at the General Motors Research Laboratories, has been used extensively in engine research studies at GMRL, at various universities and at other industrial research labs. This sampling valve has been described in detail in previous publications [10,11], so a discussion of it is not included here. It is important to note, however, that for the present experiments, the valve was operated with a sampling period of about 1.25 ms which corresponds to a time resolution of about 4 to 5 crankangle degrees at 600 rpm. The sampling valve had an orifice diameter of 1.0 mm and was inserted 2.0 mm into the combustion chamber. For the maximum cylinder pressure at which we sampled end gas, a sample volume of about 1 ml was obtained each time the valve was actuated. This corresponds to a sampling sphere of influence of approximately 4 mm radius. Based on this calculation, any dead volume or boundary layer effects on the sampled gas are estimated to be negligible for the whole range of cylinder pressures used for sampling. In addition, the positioning of the sampling orifice of the valve was such that the sample was obtained from the center of the end-gas region, far from the head surface and piston dome.

Once the end gas samples were withdrawn from the engine through the sampling valve, the samples flowed through a teflon transfer line, to a syringe adaptor, and then to a bubble flow meter. This transfer line was heated to 50°C to prevent condensation and dropout of water vapor and aldehydic species. A portion of the flowing end gas samples were collected in 500 μ l gas syringes through the syringe adapter, and stored in an oven at 50°C for later chromatographic analysis. A minimum of 3 minutes of sampling at any given engine condition and/or sampling crankangle was allowed prior to collection of the syringe samples, in order to allow the sample valve and transfer lines to be fully purged and equilibrated.

The chromatograph used for species analysis was a Hewlett Packard 5840A temperature programmable unit, equipped with an 1.8 m by 3 mm, 80/100 mesh "Porapak Q" column and flame ionization detector (FID). In addition, the instrument was outfitted with a post column nickel catalyst reactor operated at 335°C with an auxiliary hydrogen supply. This reactor methanizes CO and CO₂, making them detectable with the FID, and also scavenges the oxygen from oxygenated species, such as aldehydes and alcohols, making them more sensitive to FID detection. The chromatographic operating conditions were: helium carrier- 30 cc/min; H₂ to FID- 30 cc/min; air to FID- 250 cc/min; H₂ to catalyst- 30 cc/min; temperature program- 35°C for 5 min., 20°C/min to 180°C, 180°C for 7 min; sample size- 200 μ l at 1 atm. Identification and quantification of species was accomplished using standard gas mixtures and specially prepared head gas samples for the heavier materials. Separate gas-chromatograph/mass-spectrometer (GC/MS) analysis was carried out to verify the gas standard identifications, to identify initially unknown peaks, and to identify overlapping species.

SAMPLING VALVE CALCULATIONS

The gas sample which is extracted from the engine can undergo further reaction in the valve, and this could result in significant uncertainties in the measured concentrations of stable species. A detailed chemical kinetic model of reactions occurring in the sampling valve was formulated to assess the effect of continued reactions in the valve. In the sampling valve, the gases expand rapidly through a sonic orifice to a relatively low temperature and pressure, shock back up to nearly the original temperature so as to match the probe exit pressure condition, and then cool convectively in the valve and transfer lines. The time required for the initial expansion and shock recovery is only a few microseconds. Thus, the sampled gas undergoes a brief, downward spike in temperature before being convectively cooled in the sampling valve.

In the simplified model of the valve, the brief downward spike in temperature was ignored since its duration is so short (approximately 1-2 μ s) that its effect on the overall extent of reaction is small. Neglect of this temperature spike tends to place an upper limit on the calculated influence of reactions occurring in the valve. The gas temperature was assumed to drop linearly from the inlet temperature to the approximate exit temperature of 400 K in 6 ms, which is the residence time for the gas sample in the valve. This is a conservative estimate of the valve's cooling ability because the actual temperature history would exhibit exponential behavior rather than the assumed linear behavior and would give more rapid cooling of the gas sample. Since the pressure drops almost instantaneously from the high pressure in the engine to about 1 atm in the valve, the entire calculation was performed at 1 atm. The detailed

chemical kinetics mechanism described later in the paper was employed in these calculations. The model calculated the variations in species concentrations with time as the gas sample proceeded through the valve.

Calculations were performed for gas samples taken from the end gas at various times and for samples extracted at various temperatures. The species concentrations used to represent the end-gas sample were obtained from the autoignition calculations for n-butane/air mixtures which are described later. Calculated concentrations were used rather than those measured since the former included all the required radical species. Calculated results for a sample extracted from the end gas at 1000 K are shown in Fig. 1. The gas sample was extracted from the end gas at the time when the fuel concentration had dropped to half its initial value. At this time in the autoignition process, the fuel and its intermediates are reacting vigorously and may continue to react significantly when they enter the sampling valve. In Fig. 1, the fuel concentration in the valve drops by approximately two percent of its original value. Most of this change occurs during the first millisecond when the temperature in the valve is in the range of 900-1000 K. The OH concentration (which is typical of other radicals such as H, CH₃, C₂H₃, C₂H₅, and C₄H₉) decays rapidly during this time. Calculations of the gas sample in the valve were performed for samples extracted from the end gas when the fuel had dropped to 75%, 50%, and 25% of its initial value and at extraction temperatures of 1000 and 1100 K. For all gas samples extracted at 1000 K, concentrations of the fuel and stable intermediates were calculated to change by less than $\pm 15\%$ due to continued reaction in the valve. Most of the concentration measurements reported later in the paper were taken at temperature below 900 K, except for the one measurement point closest to the knock point.

Therefore, continued reaction in the valve should not affect the stable species concentrations significantly for most of the measured concentrations. Also, these concentration changes resulting from continued reaction in the valve are less than other estimated uncertainties in the measured species concentrations due to cycle-to-cycle variations and gas analysis.

EXPERIMENTAL RESULTS

The chromatograms illustrated in Fig. 2 represent the analyses of end gas samples extracted from the engine while operating with n-butane under knocking and nonknocking conditions. The position of the peaks along the abscissa is a measure of the column retention time for the particular species represented by that peak, and the area under each peak is directly related to the concentration of the species. The sample composition shown in Fig. 2 (top) corresponds to end gas conditions just prior to autoignition and knock (3.2 ms after TDC ignition at 600 rpm, 160°C and 1.53 atm inlet conditions, and $\phi = 1.0$). By reducing the inlet manifold pressure to 1.20 atm with all other conditions remaining fixed, the time of autoignition was delayed to the point where normal flame propagation just consumed the last of the end gas before autoignition would have occurred, resulting in the nonknocking operating condition. The chromatogram in Fig. 1 (bottom) illustrates the stable species composition of the end gas just prior to flame arrival for the nonknocking case (3.9 ms after TDC). A comparison of the two cases in Fig. 2 reveals that the same species are present in the end gas whether or not knocking occurs. The difference, however, is that the concentrations of some species are significantly higher in the knocking case than in the nonknocking case, indicating that

the low temperature reactions in the end gas are proceeding further under knocking conditions. This is particularly evident for the propene, butene, acetaldehyde, and methanol. The significance of these species and their associated reactions to the autoignition process is discussed later.

Data of the type illustrated in Fig. 2 were collected as a function of time during the end gas compression. Figures 3-7 show these data plotted as concentration versus time from top dead center, and compare the knocking and nonknocking cases directly. A significant feature of these data is the observation that the concentration levels of the intermediate species do not begin to increase from their background levels until late in the compression stroke, about 5 ms or 15 crank angle degrees before TDC. Notice also that, consistent with this, the fuel concentration begins to drop at the same time. These observations indicate that the low temperature oxidation reactions in the end gas are not occurring to a significant extent until quite late in the compression heating of the end gas.

In a companion set of experiments, end gas samples with the engine running on iso-butane were collected in order to investigate the effects of fuel molecular structure. As noted, the manifold inlet conditions were increased to 210°C and 1.79 atm for knocking conditions and 190°C and 1.79 atm for nonknocking conditions. Figure 8 shows the chromatograms for samples taken just prior to autoignition for the n- and iso-butane fuel cases. Comparison of the chromatograms illustrates some of the differences in the low temperature oxidation chemistry between straight chain and branched chain hydrocarbon fuels. Specifically, it is seen that when running on iso-butane, the concentrations of methane, ethane, and propene are higher just prior to autoignition than that when running on n-butane.

On the other hand, ethene, methanol, and acetaldehyde are present in significantly lower concentrations. Also, a totally different group of higher hydrocarbons (yet to be identified) is found in samples obtained when running on iso-butane. Concentration data as a function of time relative to TDC for the knocking iso-butane runs are presented in Figs. 9-12; selected points indicating species concentrations for the nonknocking iso-butane cases are included as well.

NUMERICAL MODEL AND CHEMICAL KINETICS MECHANISM

The computer modeling portion of this study was carried out using the HCT program [12], which solves the coupled chemical kinetics and energy equations. The main portion of the detailed reaction mechanism employed in the calculations has been developed and validated in a series of previous studies [13,14]. Reverse reaction rates are computed from the forward rates and the appropriate thermodynamic data [15,16,17]. This mechanism has been shown to describe the high temperature oxidation ($T > 1000$ K) of n-butane, propane, propene, ethane, ethylene, acetylene, methane, methanol, carbon monoxide and hydrogen over a wide range of experimental conditions.

During the engine cycle, the end gas is subjected to temperatures in the range of 450 K to 700 K for a considerable length of time (as long as 40 ms at the engine conditions discussed in this work). Additional reactions that may make significant contributions when the end gas is in this temperature range have been added to the above mechanism. These reactions mainly involve the addition of oxygen to alkyl radicals and their subsequent production of hydroperoxides which decompose and provide chain branching. These additional reactions are tabulated and discussed in References 18 and 19 where the oxidation of acetaldehyde and propene are

treated. The present combined mechanism correctly predicts acetaldehyde oxidation in static reactors [18] and rapid compression experiments [20]. Prediction of propene oxidation in static reactors [19] ($600 < T < 700 \text{ K}$) is in progress.

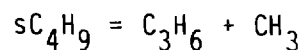
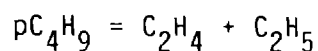
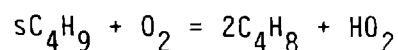
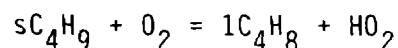
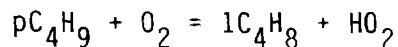
With the above mechanism, the model simulates the thermochemical history of the end gas in the combustion chamber, using the experimentally measured temperature and pressure. The calculation starts at 23 degrees before TDC which is the time of the first available temperature measurement. The model follows the measured temperature up to the experimental knock point which is the point just before the measured temperature and pressure rise sharply at autoignition. After this time, the temperature is determined from heat release in the mixture and compressional heating and cooling as calculated from the measured pressure. This modeling treatment was employed productively in previous work [21].

MODELING RESULTS

Modeling simulations of the chemical reactions occurring in the end gas were performed for both n-butane and iso-butane. For n-butane, the calculated concentrations of olefins are shown in Fig. 13 and the aldehydes in Fig. 14. The first olefin to evolve (Fig. 13) is butene which is plotted as the combined concentration of $1\text{C}_4\text{H}_8$ and $1\text{C}_4\text{H}_8$, followed by ethene and propene. This is the same behavior as seen in the measured concentrations of olefins in Fig. 3. The measured concentrations are only available at early times because it was not possible to sample at times too close to autoignition. If it were possible to sample at times very near autoignition, the measured concentration histories would be expected to

peak and fall as the calculated concentrations. It is of interest to examine the ordering of the olefins with respect to concentration during the time before they reach their maximum values, at which time data are available for comparison. For the calculated olefins at any given time up to the maximum concentration point (approximately 3.2 ms after TDC), their ranking by concentration is butene, ethene, and propene (Fig. 13). This is the same ranking as seen in Fig. 3 for the measured concentrations.

The model predicts that substantial amounts of 1-butene and 2-butene are produced, consistent with the experimental data (Fig. 3). This is of interest since neither experimental results nor calculations [13] indicate that significant amounts of butenes are produced by n-butane oxidation in a turbulent flow reactor at 1100 K and atmospheric pressure. These differences in butene production are attributed to the competition between butyl radicals reacting with O_2 and their decomposition:

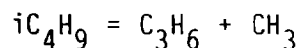


At the lower pressure and more dilute conditions of the flow reactor, thermal decomposition is the predominant route. At the higher pressures (20-30 atm) and less diluted conditions of the end gas, the butyl radicals are primarily consumed by O_2 , which yields butene. The characteristic temperatures are actually similar in these two environments so that they are not an important factor in explaining these differences. The characteristic temperature in the end gas simulations is approximately 1120 K which occurs when the fuel concentration has dropped to half its

initial value. In the flow reactor, the characteristic temperature is approximately 1130 K for the near stoichiometric cases.

Figure 14 gives the modeling results for the aldehydes in the case of n-butane oxidation. Large amounts of acetaldehyde are predicted compared to other aldehydes, and similar trends are seen in the experiment (Fig. 4.). Again, measured concentrations of aldehydes are available for comparison only during early times. Prior to the time that the maximum concentrations are reached (approximately 3.2 ms after TDC), the calculated ordering is acetaldehyde (ethanal), propionaldehyde (propanal), and acrolein (propenal). The experimental ordering (Fig. 4) shows propionaldehyde and acrolein reversed compared to the calculation, although both species are present only in minor quantities.

In the case of iso-butane, the species histories are given in Figs. 15 and 16. The results for the calculated olefins (Fig. 15) are remarkably similar to the measured ones (Fig. 9). Propene is produced in large quantities early on, and ethene is formed later in much smaller concentrations. Almost all of the propene comes from isobutyl radical decomposition:



The model predicts smaller amounts of iC_4H_8 and $1C_4H_8$ (both with peak concentrations of approximately 2500 ppm) compared to the amount of propene. The experiments in this case were not able to identify or quantify the butenes because of an inability to resolve their chromatographic peaks from that of iso-butane.

Again, the calculated aldehydes (Fig. 16) are similar to the measured ones (Fig. 10). At times prior to when they reach their maximum values, acetaldehyde has the largest concentration with propionaldehyde and

acrolein following. The experimental measurements give the same ordering, but they show relatively more propionaldehyde than the calculations.

Some species were measured but their formation and consumption were not considered in the chemical kinetic mechanism. In the case of n-butane, these species included oxirane, methacrolein, butanal, C_2H_2O , and 2-butenal. In the case of iso-butane, acetone was measured but not considered in the mechanism. However, these species were present only in minor concentrations.

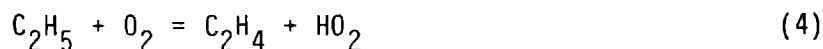
The intermediate species for both n-butane and iso-butane appear at earlier times in the measurements than in the calculations even though the predicted and measured autoignition times are nearly the same. The sampling valve has a temporal window of about 1.25 ms. This window tends to reduce the steepness of the actual concentration profiles and tends to lower the maximum measured levels, since the measured sample is representative of species concentrations averaged over a period of time. However, this time of 1.25 ms is not sufficient to account for the discrepancy in the measured and calculated times for evolution of the intermediates. Additionally, each sampling measurement was an average over many combustion events. This process also tends to blur the species concentrations in time and reduce the slope of the species curves. Finally, the discrepancy may be due, in part, to some inadequacy in the reaction mechanism. The current mechanism does not include internal H-atom abstractions of peroxy radicals which could give additional peroxides and provide more chain branching at earlier times.

The conclusions of this work are based on the discussion of the relative amounts of intermediate species found in the measurements and the calculations. These conclusions are not significantly affected by the above discrepancies.

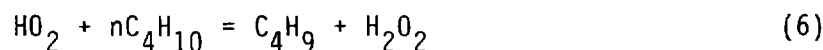
The chemical kinetics of n-butane, a straight chain hydrocarbon, was compared to that of iso-butane, a branched chain hydrocarbon, since the latter exhibits more resistance to engine knock. The fact that n-butane autoignites more readily than iso-butane can be explained in terms of the decomposition patterns of the butyl radicals. For n-butane, the primary consumption paths for the butyl radicals are



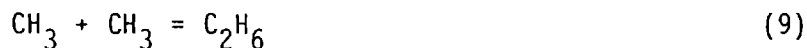
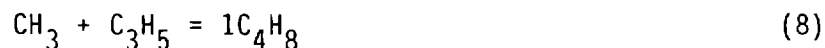
The ethyl radicals produced rapidly react with O_2



Production of H and HO_2 (reactions 1, and 3 followed by 4) is accelerating since they contribute to chain branching through the sequence



For each H or HO_2 produced, two OH can result. Most of the butyl radicals in n-butane oxidation follow accelerating paths leading to HO_2 and H radicals. A smaller fraction of the butyl radicals follow decelerating paths leading to methyl radicals (reaction 2) and chain termination



For iso-butane, most of the butyl radical consumption leads to methyl radical instead of HO_2 and H



At the time when the iso-butane concentration has dropped to half its initial value, approximately 85 percent of the butyl radicals follow the methyl route (reaction 10). At this same point in the n-butane concentration history, only 22 percent of the butyl radicals lead to the relatively unreactive methyl radical. Consequently, autoignition of n-butane proceeds more rapidly than iso-butane. This observation that iso-butane oxidation yields more methyl radicals is supported by the large fraction of propene produced both in the engine environment and the modeling simulation. If most of the butyl is thermally decomposing through reaction 10, then a large amount of propene would be expected in the intermediate products of iso-butane oxidation. Gas samples taken just prior to autoignition (final data points on Fig. 3, top, and on Fig. 9) show approximately three times more propene for iso-butane than n-butane. Modeling calculations indicate that the maximum propene concentrations for iso-butane are approximately twice that for n-butane (Figs. 13 and 15).

CONCLUSIONS

Gas samples were extracted from the end gas of a engine operating on n-butane and iso-butane under knocking and non-knocking conditions. These samples were analyzed by gas chromatography, and their concentrations were compared to those obtained from a detailed chemical kinetic model. In most cases, the relative product distributions were in good agreement between the experiment and the model. The autoignition of two isomers, n-butane and iso-butane, were compared both in the experiment and in the model in

order to better understand why branched chain hydrocarbons are more resistant to autoignition than straight chain hydrocarbons. The chemical kinetic differences in the oxidation of these two isomers was traced to the distribution of radical species that result from consumption of the various types of butyl radicals.

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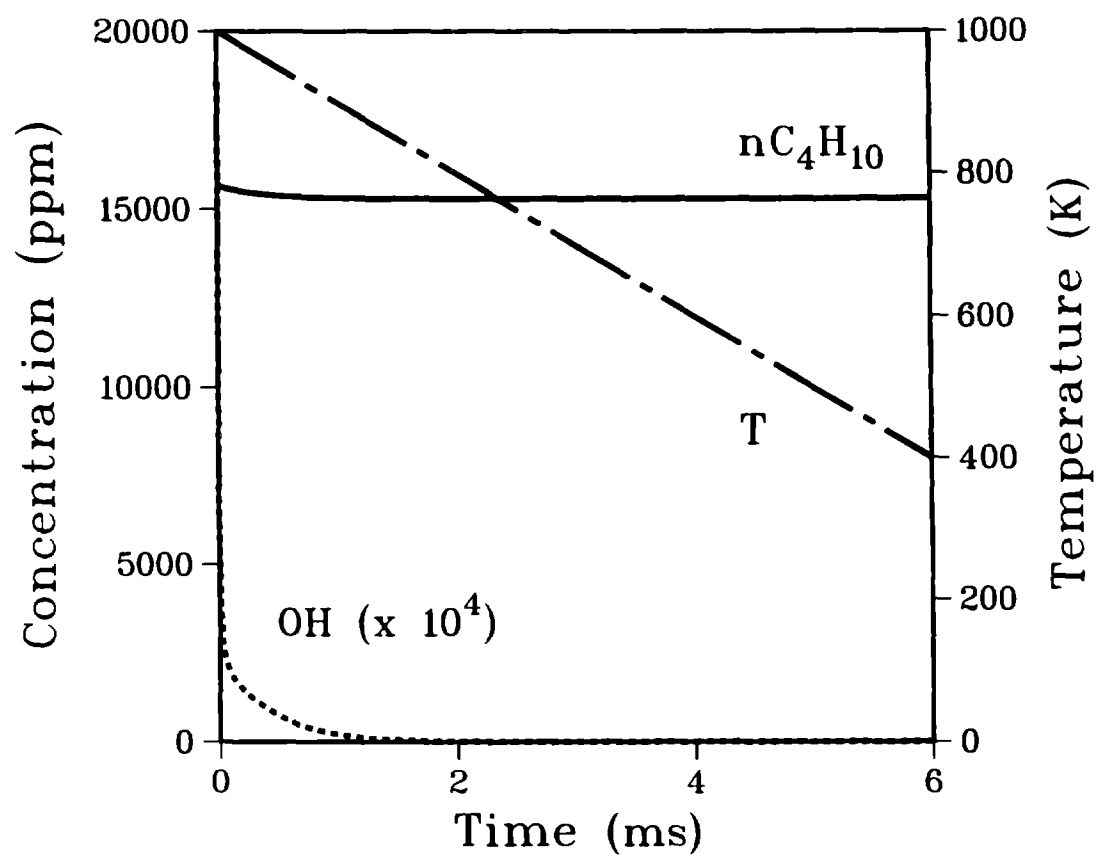


Fig. 1. The temporal history of the concentrations of n-butane and OH inside the fast-acting valve along with the temperature of the sampled gas.

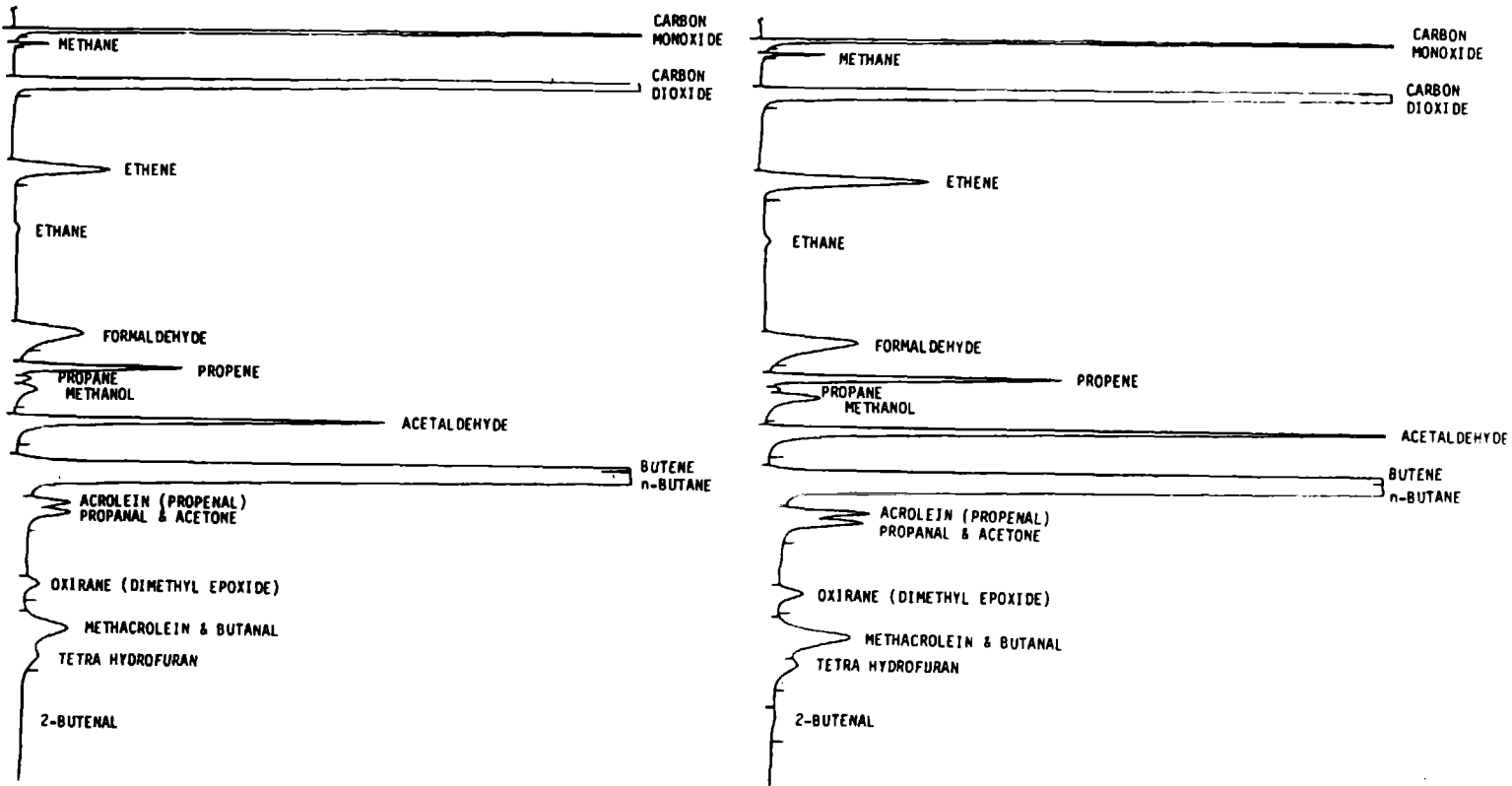


Fig. 2. Gas chromatograms of end gas samples taken just prior to auto-ignition under knocking conditions (top) and just prior to peak pressure under nonknocking conditions (bottom). Fuel, n-butane; speed, 600 rpm; manifold conditions, 1600C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

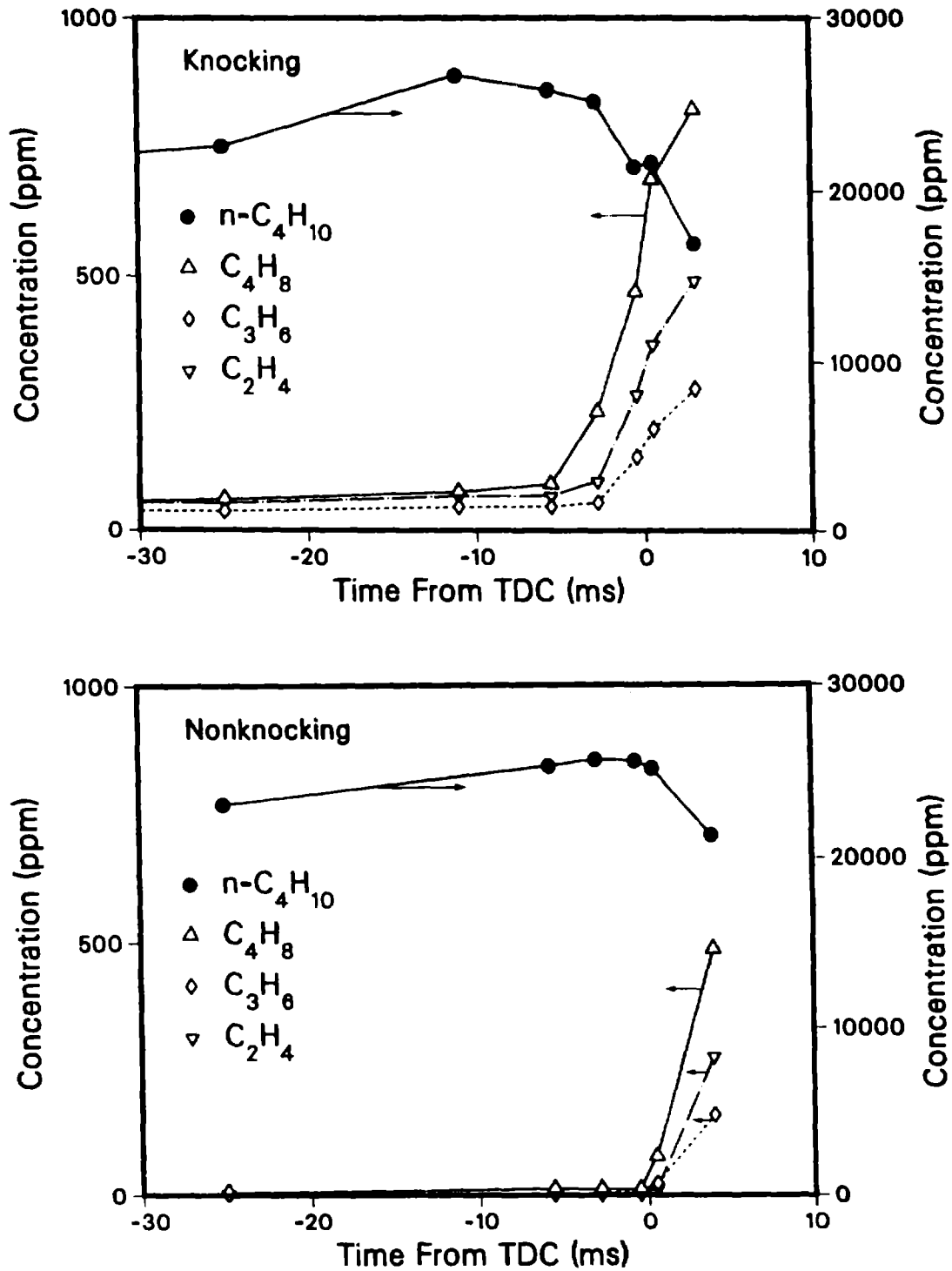


Fig. 3. N-butane and olefin concentrations measured near the end of compression with the engine operating under knocking (top) and nonknocking (bottom) conditions. Fuel, n-butane; speed, 600 rpm; manifold conditions, 160°C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

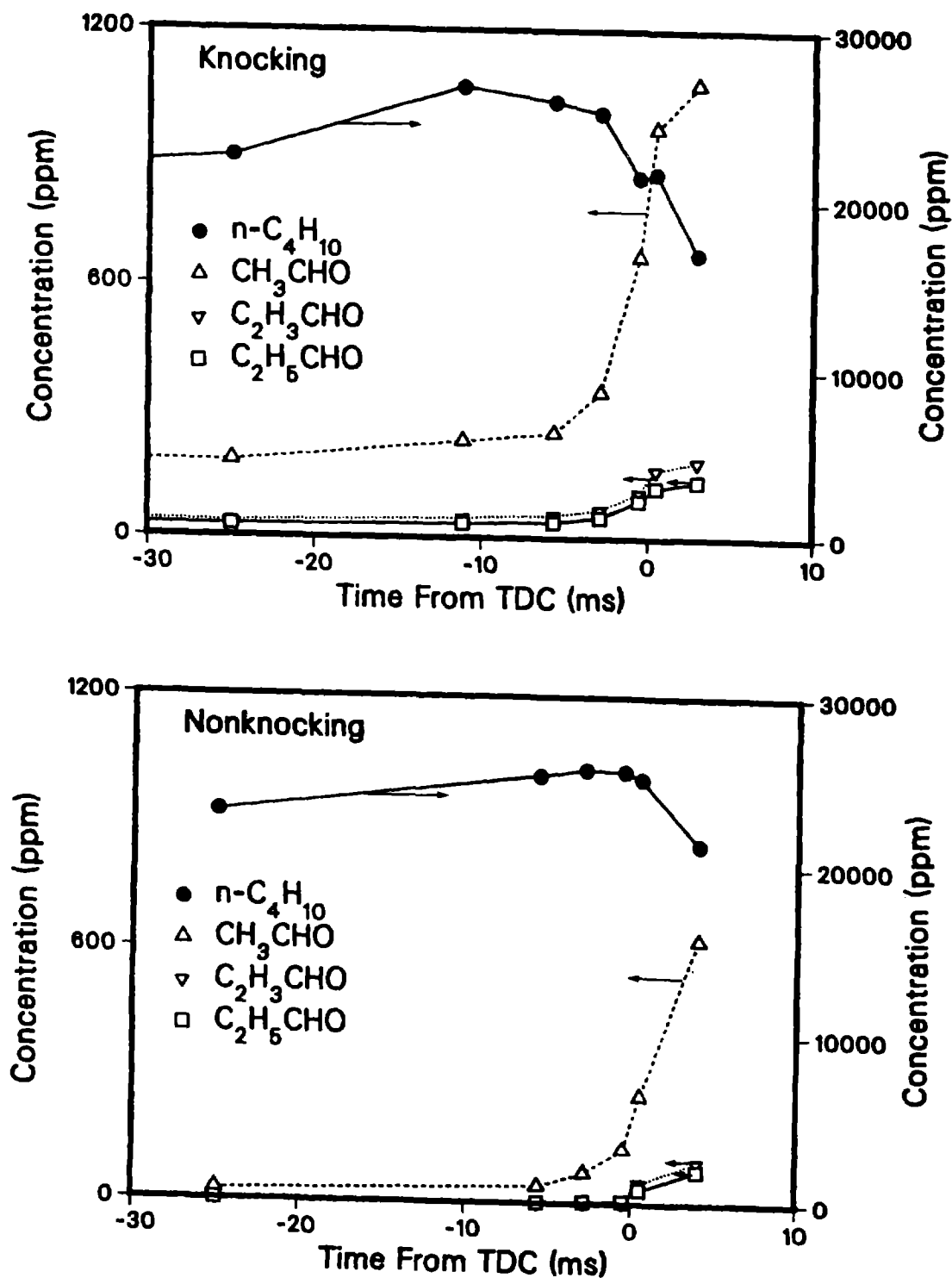


Fig. 4. N-butane and aldehyde concentrations measured near the end of compression with the engine operating under knocking (top) and nonknocking (bottom) conditions. Fuel, n-butane; speed, 600 rpm; manifold conditions, 160°C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

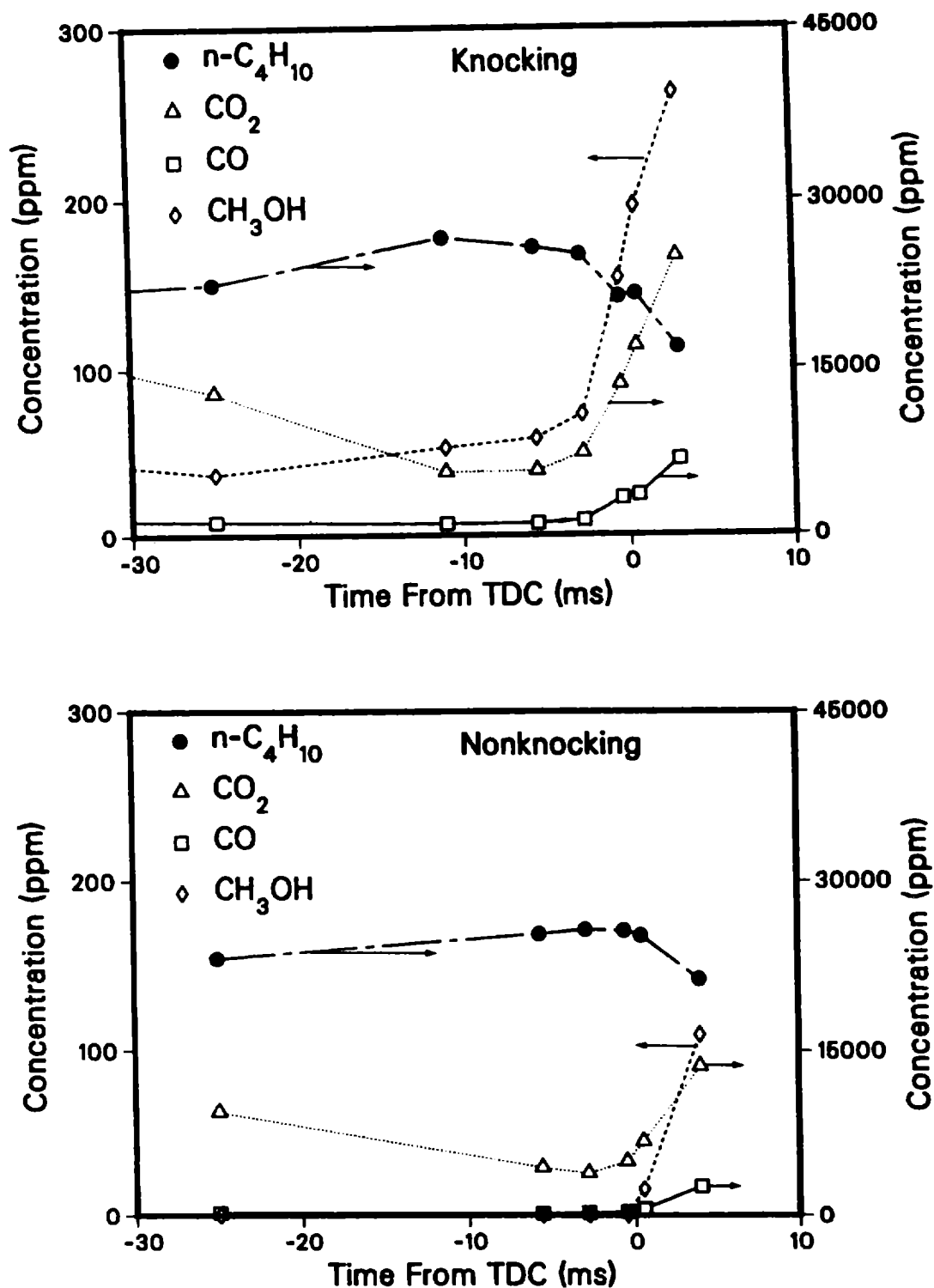


Fig. 5. N-butane, carbon dioxide, carbon monoxide and methanol concentrations measured near the end of compression with the engine operating under knocking (top) and nonknocking (bottom) conditions. Fuel, n-butane; speed, 600 rpm; manifold conditions, 160°C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

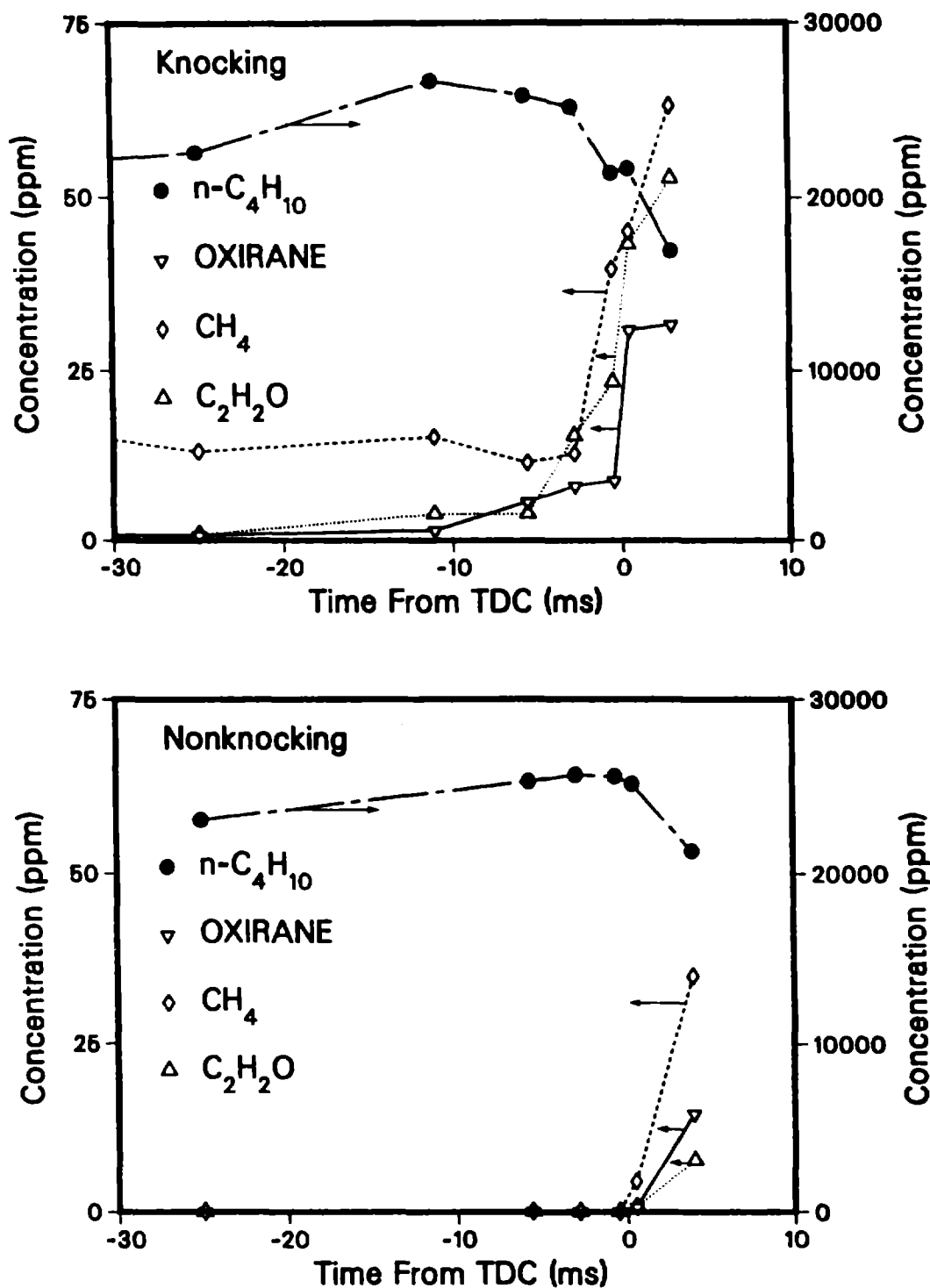


Fig. 6. N-butane, oxirane, methane and $\text{C}_2\text{H}_2\text{O}$ concentrations measured near the end of compression with the engine operating under knocking (top) and nonknocking (bottom) conditions. Fuel, n-butane; speed, 600 rpm; manifold conditions, 160°C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

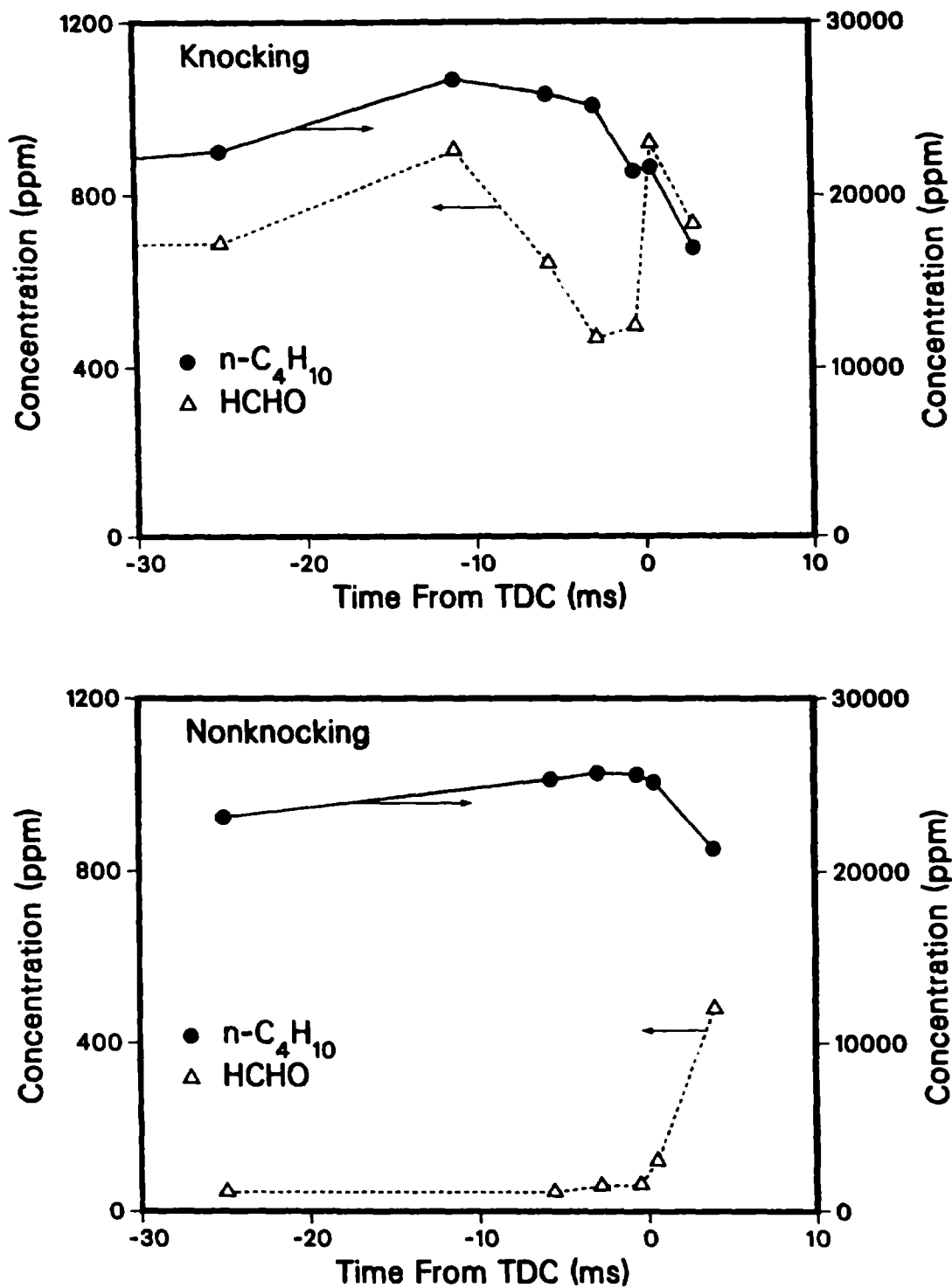


Fig. 7. N-butane and formaldehyde concentrations measured near the end of compression with the engine operating under knocking (top) and nonknocking (bottom) conditions. Fuel, n-butane; speed, 600 rpm; manifold conditions, 160°C and 1.53 atm. (knocking) or 1.20 atm. (nonknocking).

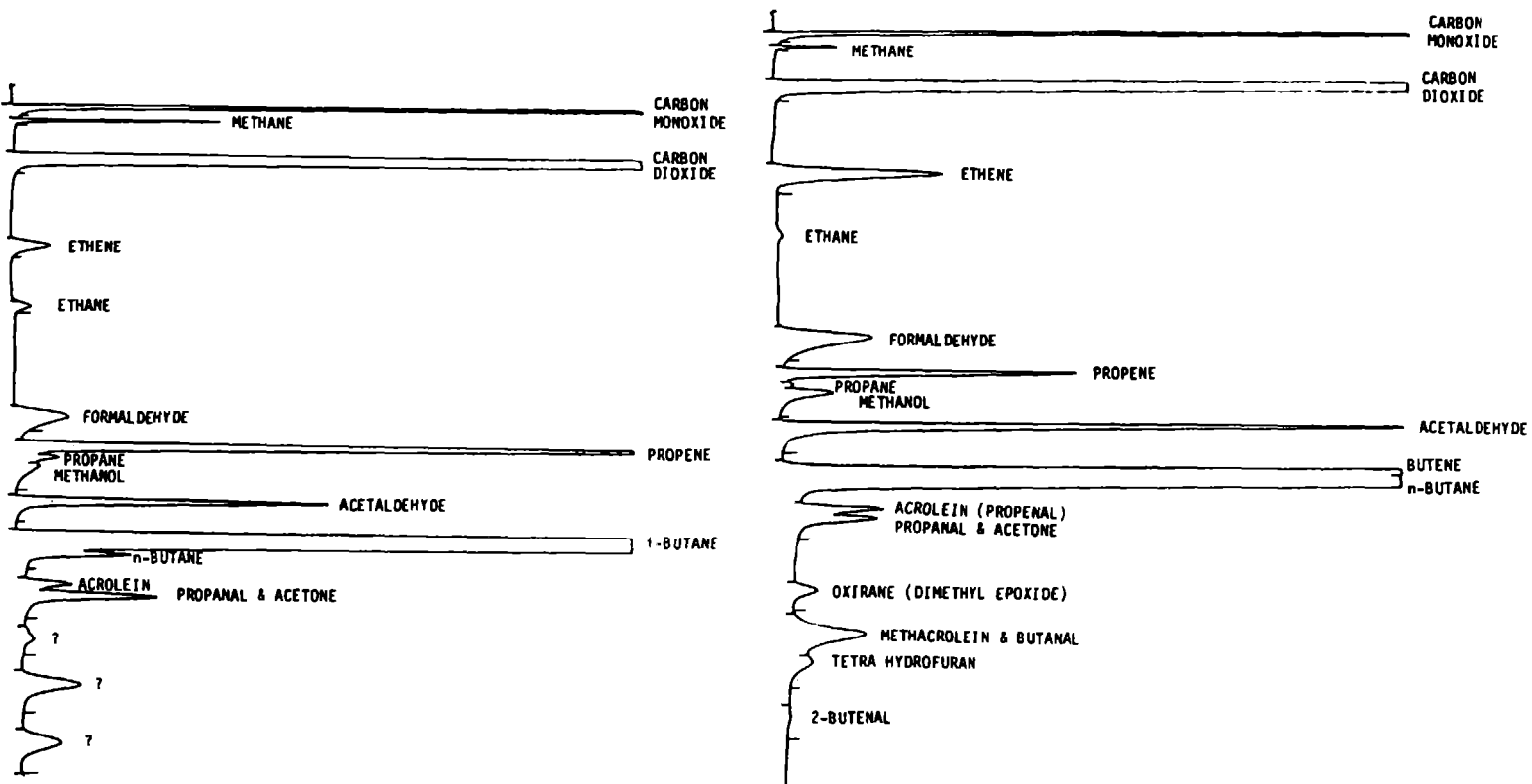


Fig. 8. Gas chromatograms of end gas samples taken just prior to autoignition under knocking conditions with the engine running on n-butane (top) or running on iso-butane (bottom). Speed, 600 rpm; manifold conditions, 1600°C and 1.53 atm. (n-butane) or 1600°C and 1.79 atm. (iso-butane).

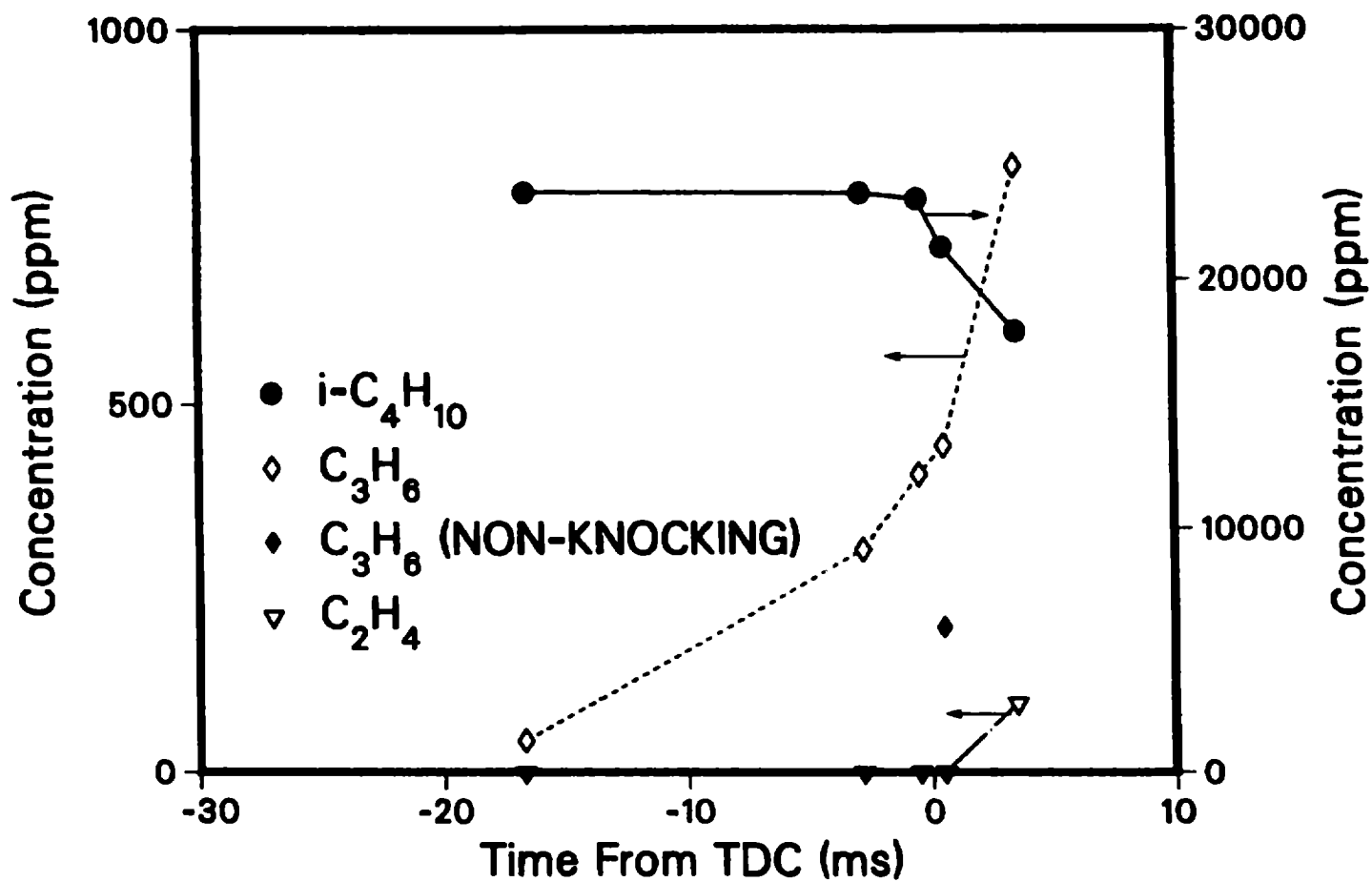


Fig. 9. Iso-butane and olefin concentrations measured near the end of compression with the engine operating under knocking conditions, and propene concentrations measured under non-knocking conditions. Fuel, iso-butane; speed, 600 rpm.

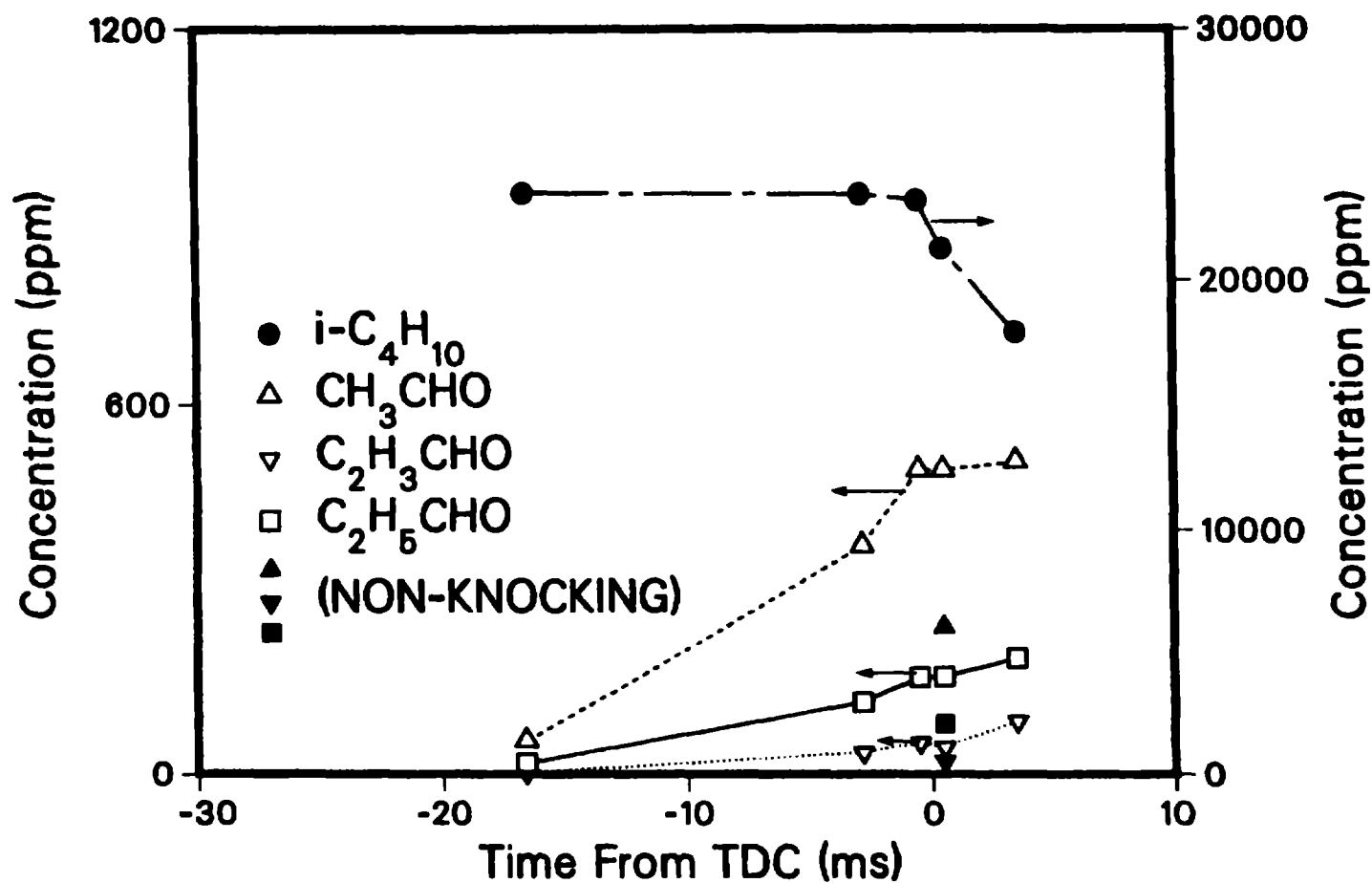


Fig. 10. Aldehyde concentrations measured near the end of compression with the engine operating under knocking and non-knocking conditions. Fuel, iso-butane; speed, 600 rpm.

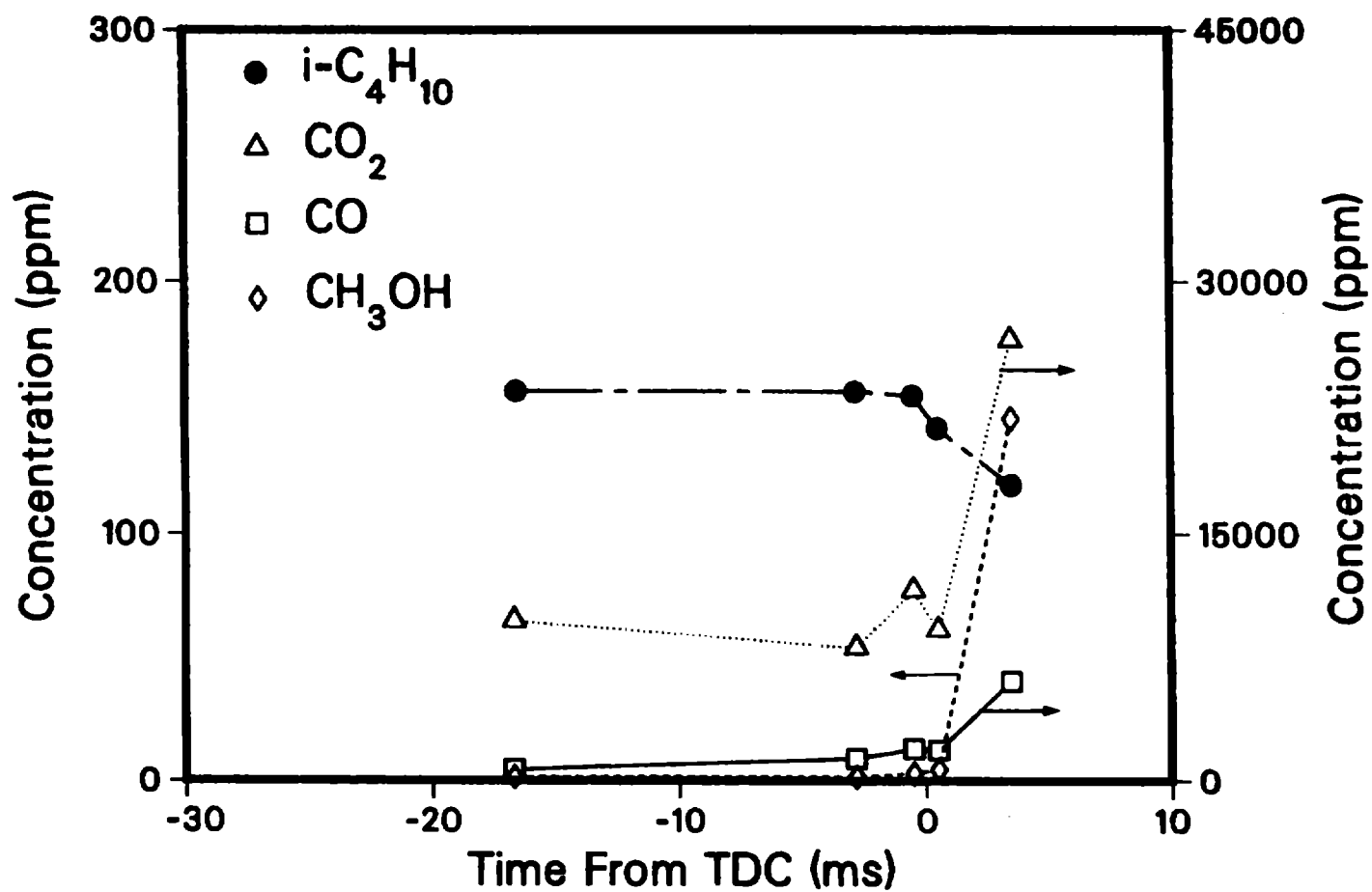


Fig. 11. Carbon dioxide, carbon monoxide and methanol concentrations measured near the end of compression with the engine operating under knocking conditions. Fuel, iso-butane; speed, 600 rpm; manifold conditions, 210°C and 1.80 atm.

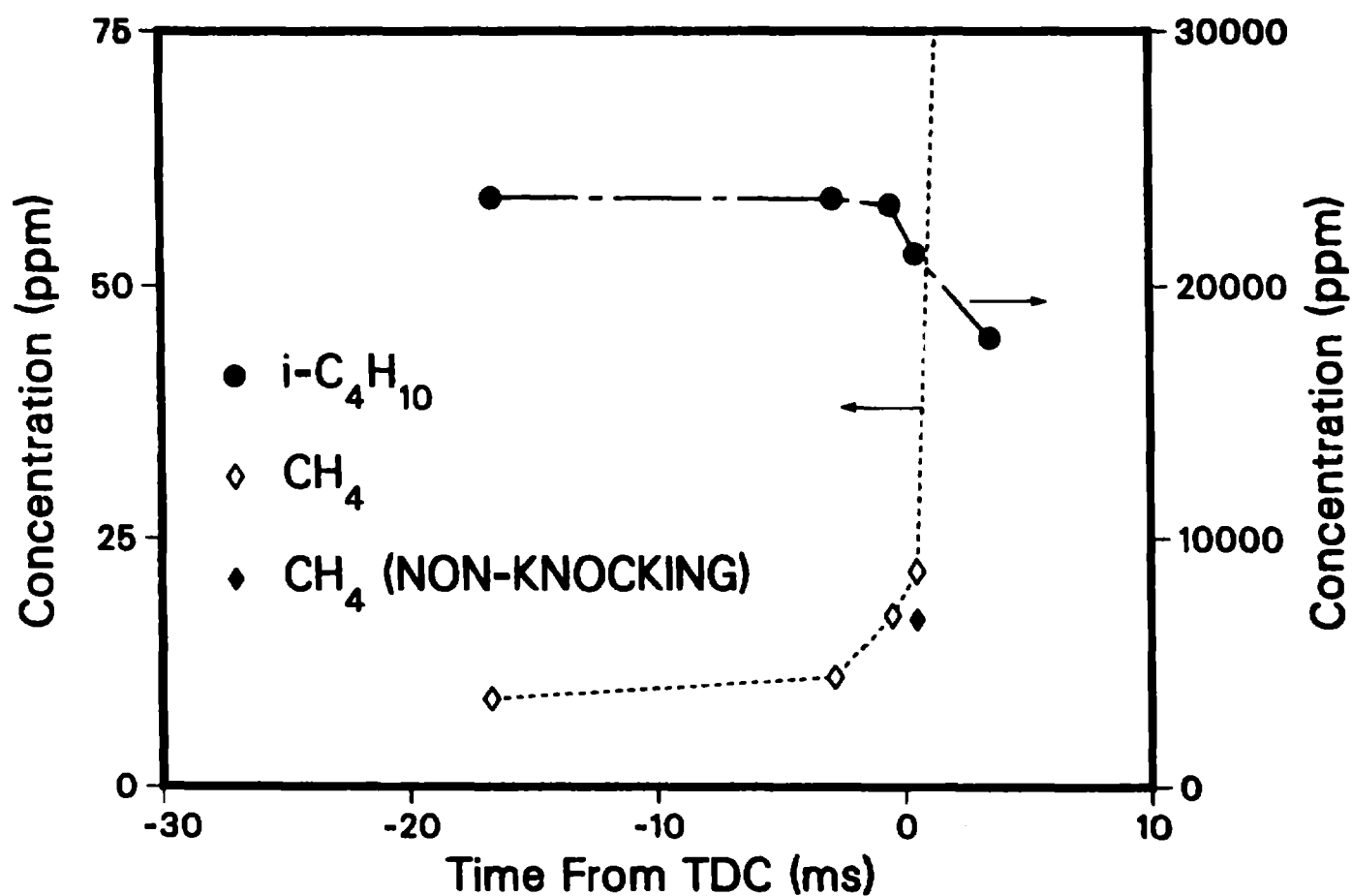


Fig. 12. Methane concentrations measured near the end of compression with the engine operating under knocking and non-knocking conditions. Fuel, iso-butane; speed, 600 rpm.

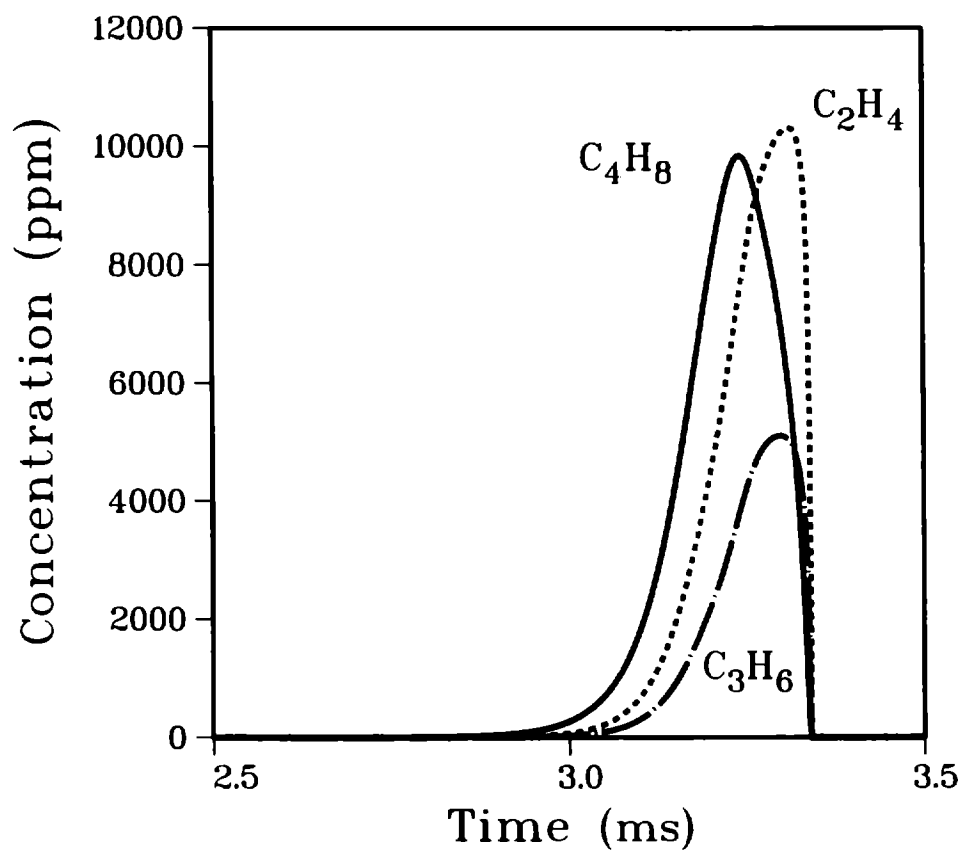


Fig. 13. Calculated olefin concentrations in the end gas for n-butane/air mixtures. Time is referenced to TDC.

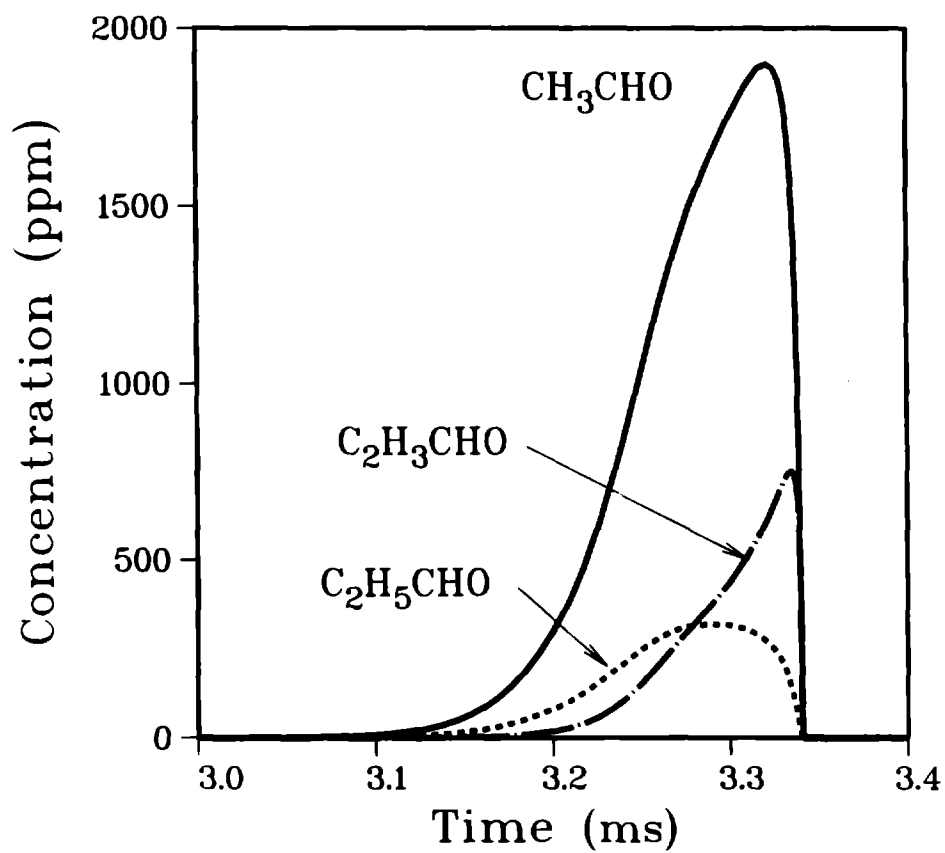


Fig. 14. Calculated aldehyde concentrations in the end gas for n-butane/air mixtures. Time is referenced to TDC.

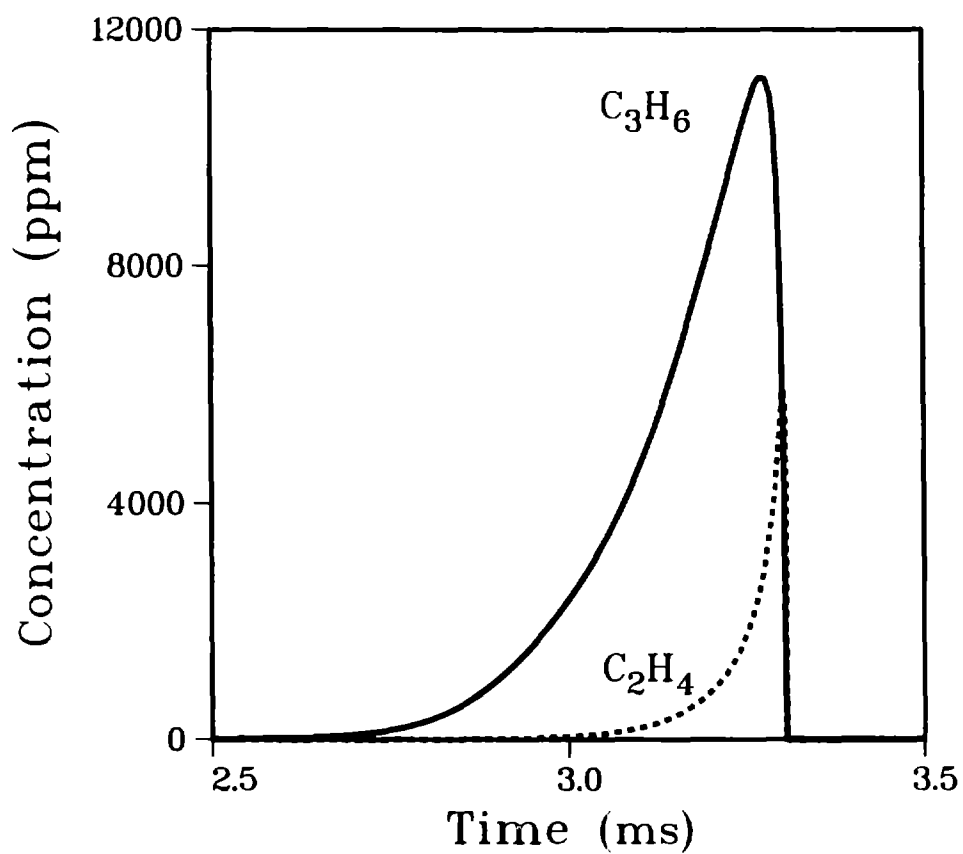


Fig. 15. Calculated olefin concentrations in the end gas for iso-butane/air mixtures. Time is referenced to TDC.

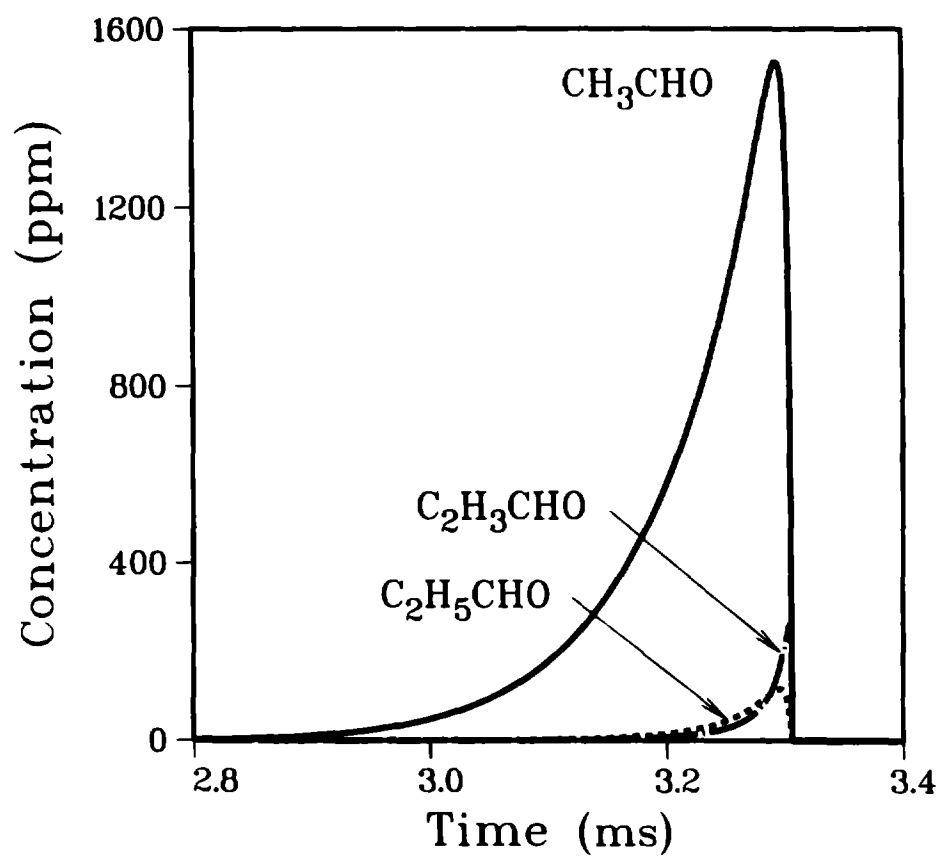


Fig. 16. Calculated aldehyde concentrations in the end gas for iso-butane/air mixtures. Time is referenced to TDC.